

A Novel Low Solvent Method for Grafting Polyaniline to Silylated Silica

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Summary: Silica gel, an important inorganic polymer with many applications, was silylated with 3-(phenylaminopropyl)trimethoxysilane (PAPTAMOS) by means of a novel “low solvent” method, whereby the silane was dissolved in a small amount of methanol, mixed with silica and reaction carried out in a heated vacuum oven. Polyaniline (PANI) was grafted to the silylated silica by *in situ* polymerization of aniline, then dedoped with aqueous ammonia. Physically adsorbed PANI was removed from the modified silica by washing with tetrahydrofuran (THF) and N-methyl-2-pyrrolidone (NMP). The silylated, PANI-modified silica had electrical conductivity $1.2 \times 10^{-3} \text{ S cm}^{-1}$ after being re-doped with methanesulfonic acid. FTIR, elemental analysis, X-ray photoelectron spectroscopy, solid-state ^{13}C and ^{29}Si NMR and morphological studies by SEM confirmed successful formation of the SiO_2 -polyaniline hybrid material.

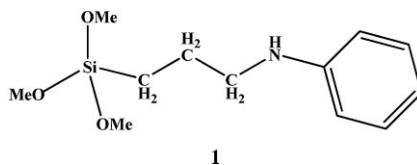
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Introduction

Conducting polymers (CPs) are speciality polymers with multifunctional properties.^[1] A route to effective utilisation of their functionality is preparation of hybrid materials, where a CP is combined with an inorganic substrate. Silica is one of the most popular substrates due to its many existing and potential applications. To combine the properties of silica and polyaniline in a single hybrid material, it is important to create a strong bond between the CP and the inorganic substrate, so that potential applications of these novel hybrid materials can be realized.

Although polyaniline (PANI) is a frequently used CP in combination with different fillers,^[2,3] direct attachment of PANI by polymerizing aniline in the presence of a substrate such as silica is relatively difficult to achieve. Coupling

agents such as silanes are widely used to effect indirect bonding.^[4–6] In terms of functionalisation of the silica surface one of the more promising silylating agent is 3-(phenylaminopropyl) trimethoxysilane (PAPTAMOS) (**1**) that has N-substituted aniline functionality.^[7]



It has been reported that for silanes, including PAPTAMOS, to react with silica a large amount of solvent, usually toluene (toluene reflux method) or methanol (for glass surface silylation) is required.^[7–10] In the present investigation a novel “low solvent” method was developed for silylation of silica gel using a very small amount of methanol as solvent, which has the advantages of both a “green chemistry” approach and a simplified procedure. The

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substituted aniline-functionalized silanized silica was used as an active template for linking to polyaniline by *in situ* polymerization of aniline monomer.

Experimental Part

Silica gel 922 (ECP-CHR Chromatography Reagent, Silae2E2457-1KG) was supplied by ECP-LTD (Auckland, New Zealand) and had the following characteristics: particle size 200–325 mesh (74–44 μm); surface area $450\text{ m}^2\text{ g}^{-1}$; pore diameter 6 nm; pore volume 0.75 ml g^{-1} . PAPT MOS, ammonium persulfate (APS), methanol, acetone, tetrahydrofuran (THF), N-methyl pyrrolidinone (NMP), hydrochloric acid and methanesulfonic acid (MSA) were all analytical grade reagents and were used as supplied by Sigma-Aldrich.

Silylation of Silica Gel

0.25 g of PAPT MOS dissolved in 1 g (about 1.25 ml) of methanol was placed in a small ceramic crucible. 1 g of silica gel that had been pre-treated by heating in a vacuum oven at 120°C for 24 h was thoroughly mixed with the PAPT MOS/methanol mixture. The crucible was covered with a ceramic lid, maintained at 70°C for 0.5 h and then heated under vacuum for 42 h at 110°C . The product was washed four times with methanol (30 ml; centrifugation, 10 min, 3000 rpm, following by decanting each time) then vacuum dried at 60°C for 16 h.

Grafting of PANI to Silylated Silica

0.5 g (5 mmol) of aniline was added with stirring to 20 ml of 1 M aqueous HCl. 0.5 g of silylated silica was dispersed in the aniline solution with continuous magnetic stirring, and 1.37 g (6 mmol) of APS, dissolved in 10 ml of water, was added dropwise over a period of about 30 min at ambient temperature. The resulting mixture was continuously stirred for 5 h at ambient temperature, then centrifuged, and the precipitate separated by decanting the supernatant. The precipitate was washed

three times with water (30 ml, centrifugation-decanting, 3000 rpm, 7 min. each time). After the final decantation the solid product was dedoped by continuous stirring overnight with 30 ml of 2.8% aqueous ammonia. The purpose of dedoping was to ensure that free (i.e. non-grafted) PANI was converted to the emeraldine base (EB) form the oligomers of which are soluble in THF, and non-oligomeric PANI is soluble in NMP, whereas the emeraldine salt (doped) form is insoluble. The solid product was then washed consecutively with water to remove water-soluble impurities; THF and NMP to remove PANI that was not bonded to silica; and acetone to remove residual THF and NMP. The dedoped product containing grafted chains of PANI in the EB form was vacuum dried for 24 h at 40°C .

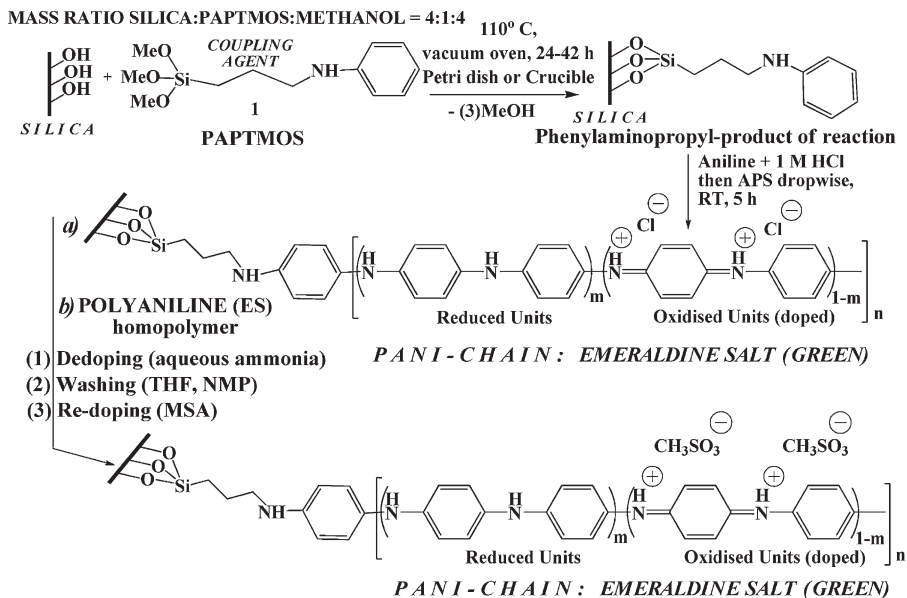
Re-Doping of SiO_2 -PANI (EB) Hybrid

The purpose of re-doping was to convert the PANI chains in the hybrid material to the conductive emeraldine salt (ES) form. The hybrid material (0.5 g) was suspended in 20 ml of 1 M aqueous MSA with magnetic stirring. The reaction mixture was continuously stirred overnight at ambient temperature, then centrifuged and the supernatant decanted. The solid product was washed with water and acetone, then vacuum dried at 50°C for 20 h.

The overall process (assuming complete de-methoxylation of PAPT MOS) is shown in Scheme 1.

Results and Discussion

The silylation reaction was carried out at 110°C to allow comparison with the toluene reflux method. The reaction time of 42 h was used to optimise the extent of reaction. A possible mechanism for the silylation of silica with 3-aminopropyltriethoxysilane (APTES) has been proposed.^[7] We envisage that the reaction of silica with PAPT MOS occurs in a similar fashion, as indicated in Scheme 1. The appearance of major diagnostic bands for



Scheme 1.

aromatic ring groups (1601 and 1503 cm^{-1}) of the aniline function in the silane treated silica indicates that silica gel was successfully silylated (Figure 1a). After grafting PANI to the silylated silica and isolation of the product, diagnostic bands at 1598 and 1509 cm^{-1} , characteristic of the quinonoid form and benzenoid rings of PANI, appeared in the FTIR spectrum (Figure 1b, spectrum 1), and the Si–O–Si–Si band at 1070 cm^{-1} was largely unaffected, except for the more prominent shoulder on the high wavenumber side of that band, in the spectrum of the silylated silica. The shoulder is attributed to the Si–O–Si band of the silyl moiety. Re-doping the PANI chain with MSA was confirmed by the FTIR spectrum (Figure 1b, spectrum 2) in which the aniline bands shifted by about 9 cm^{-1} , which is typical for conversion of the undoped emeraldine base to the doped emeraldine salt form of polyaniline. The appearance of the broad peak in the region 3700 cm^{-1} to 3000 cm^{-1} in Figure 1b is due to the grafting of PANI containing N–H groups onto silica.

Elemental analysis data are given in Table 1. The C:N atomic ratio (9.99:1)

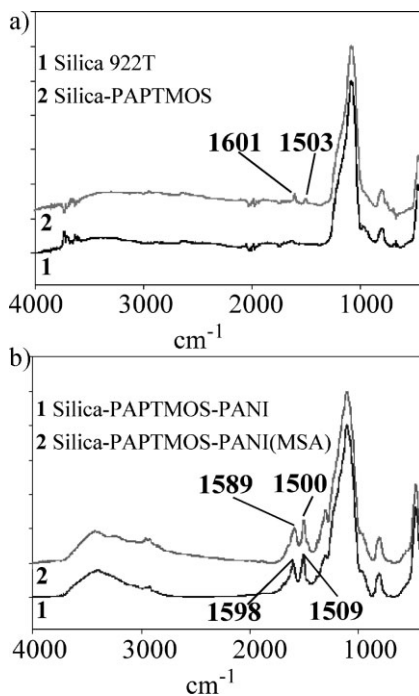


Figure 1.

FTIR spectra of a) silica gel 922 and the product of its silylation; b) dedoped silica-PANI hybrid and its emeraldine salt form doped with MSA.

Table 1.

Elemental analysis data and derived atomic ratios for the reaction products.

COMPOUND	C, %	H, %	N, %	S, %	C:N, atoms	N:S, atoms
Silica-PAPTOS	9.56	1.47	1.11	–	9.99:1	–
Silica-PAPTOS-PANI	19.35	2.08	3.57	–	6.33:1	–
Silica-PAPTOS-PANI-MSA	19.88	2.36	2.77	0.96	8.36:1	6.60:1

found for the product of silica silylation is somewhat higher than for PAPTOS (9:1). The discrepancy can be accounted for by incomplete reaction of the methoxy groups of PAPTOS with silica; the atomic ratios suggest >90% reaction.

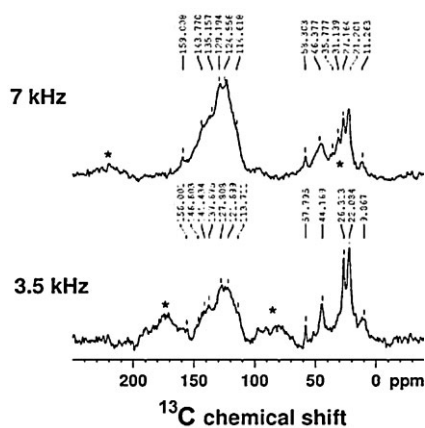
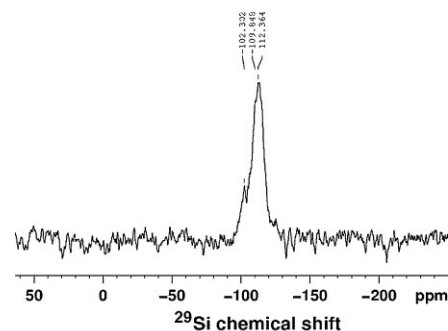
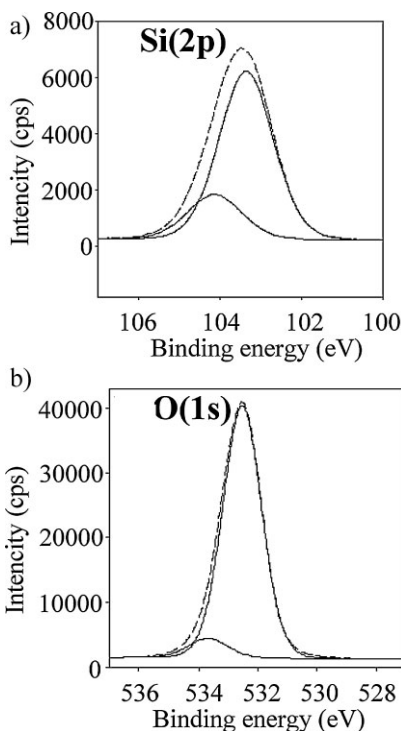
With the simplifying assumption that the silylated silica (Silica-PAPTOS) comprises SiO_2 and silyl moieties (i.e. PAPTOS molecules from which three

CH_3O groups have been eliminated), the elemental analysis data indicate that the silylated silica was about 86 wt% silica and 14 wt% silyl moiety. That composition corresponds to about 94 mol% SiO_2 . The degree of grafting, $\text{DG}(\%)$, defined by

$$\text{DG}(\%) = 100 \times (m_f - m_0)/m_0$$

where m_0 and m_f are the initial mass of silica gel and the mass of silylated product, respectively, was 16.3%.

With the same assumption, the composition of the Silica-PAPTOS-PANI product was 74.6 wt% SiO_2 , 4.5 wt% silyl

**Figure 2.** ^{13}C NMR spectra of Silica-PAPTOS-PANI (EB).**Figure 3.** ^{29}Si NMR spectrum of Silica-PAPTOS-PANI (EB).**Figure 4.**

XPS deconvoluted spectra for Silica-PAPTOS product (a) Si, (b) O.

moiety, and 20.9 wt% aniline (as PANI chains). It is interesting to note that in this product the SiO₂/PAPTMOS moiety molar ratio was about 45, whereas the corresponding molar ratio in the Silica-PAPTMOS product was about 16. It appears therefore, that in the course of formation of the polyaniline chains a significant proportion (of the order 70%) of the silyl moieties that had been bonded to the silica surface was displaced. We speculate that the initial silylation predominantly activates the silica surface and facilitates direct reaction of aniline with the substrate.

¹³C NMR Spectroscopy

In addition to the characteristic peaks for PANI, (110–160 ppm) the ¹³C spectrum (Figure 2) exhibits peaks in the aliphatic region. The assignment of the latter peaks as follows.^[11] SiCH₂(I)CH₂(II)-CH₂(III)NH: C(I) = 9–11 ppm; C(II) = 20–27 ppm; C(III) = 44–46 ppm; CH₃O = 49–57 ppm. The peaks in the aliphatic region

(50–10 ppm) suggest that the coupling agent has been introduced into the structure. Also, the relatively weak peak of methoxy group (around 50 ppm) confirms (as noted above) complete de-methoxylation of PAPTMOS did not occur.

²⁹Si NMR Spectroscopy

The ²⁹Si NMR of Silica-PAPTMOS-PANI (EB) is shown in Figure 3. The two resonances observed were assigned^[11] as follows: (a) a predominant peak at –112 ppm, *Si(OSi≡)₄; (b) a less intense peak at –102 ppm, (HO)*Si(OSi≡)₃. These are characteristic of a silica structure. The shoulder at –109 ppm indicates that there could be some Si nuclei with different coordination.

XPS Data

Survey scan from 0–1300 eV is obtained to determine the elements present at or near the surface of the silylated silica (Silica-PAPTMOS). The binding energy scale of

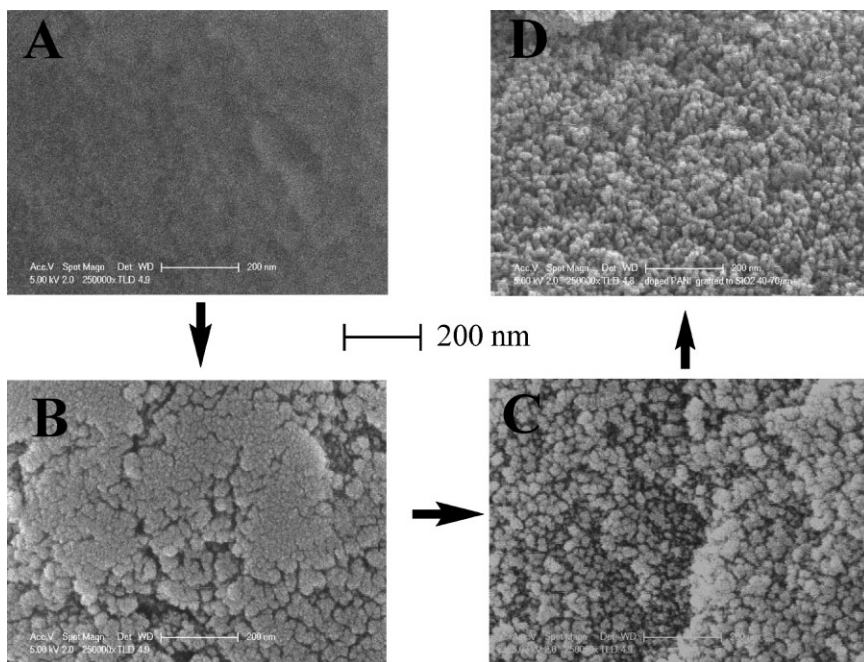


Figure 5.

SEM images of silica and products (magnification $\times 250000$): A – silica gel 922, B – silylated silica, C – Silica-PAPTMOS-PANI dedoped, D – Silica-PAPTMOS-PANI hybrid doped with MSA.

all spectra are calibrated such that the peak maximum of the C(1s) spectrum was located at 284.6 eV. Deconvolution of the Si(2p) peak gives rise to major peak at 103.3 eV and a small peak at 104.1 eV (Figure 4a). The peak at 104.1 eV confirms the presence of Si-O linkages on the substrate surface. The peak binding energies due to O(1s) for the silica sample are observed in the 530–535 eV region, where the peaks at 532.6 eV and 533.7 eV are due to Si–O–Si and Si–O–C respectively (Figure 4b)^[6]. A weak peak at 399.4 eV attributed for N(1s) from PAPT MOS moiety was also clearly seen.^[12] Presence of carbon was observed at 282–288 eV region with peak maxima at 284.6 eV.

The conductivity (σ) of the final product, Silica-PAPT MOS-PANI hybrid doped with MSA, was measured by the four-point probe method as $(1.2 \pm 0.1) \times 10^{-3} \text{ S cm}^{-1}$ at ambient temperature, whereas the unmodified silica is a non-conductor.

The SEM images shown in Figure 5 show a change of the relatively smooth surface of silica (Figure 5 A) to a surface coated with silane (Figure 5 B), and the PANI (EB)-coated surface. The final (conductive) hybrid (Figure 5 D) has an even layer of PANI emeraldine salt with spherical particles mostly 15–20 nm and up to 40–50 nm in diameter. It has similar morphology to the dedoped PANI form (Figure 5C).

Conclusion

Silica has been successfully silylated with PAPT MOS by means of a “Low Solvent Method”. PANI was grafted to the silylated silica. The hybrid material obtained by this method has shown significant electroconductivity. The method is being applied in our laboratory to other oxide and silicate surfaces.

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